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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

ELLIS et al

Atty. Ref.: 608-312

Serial No. Unassigned

Group:

Filed: September 28, 2001

Examiner:

For: OXIDATION PROCESS FOR THE PRODUCTION OF  
ALKENES AND CARBOXYLIC ACIDS

\* \* \* \* \*

J1017 U.S. PTO  
09/964849  
09/28/01

September 28, 2001

Assistant Commissioner for Patents  
Washington, DC 20231

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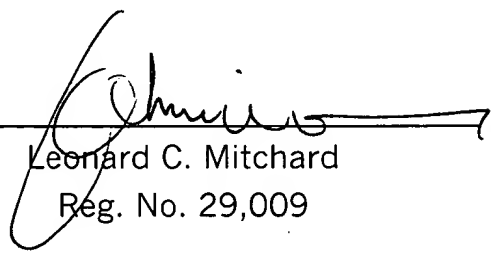
It is respectfully requested that this application be given the benefit of the foreign filing date under the provisions of 35 U.S.C. §119 of the following, a certified copy of which is submitted herewith:

<u>Application No.</u>	<u>Country of Origin</u>	<u>Filed</u>
0026243.6	Great Britain	26 October 2000

Respectfully submitted,

**NIXON & VANDERHYE P.C.**

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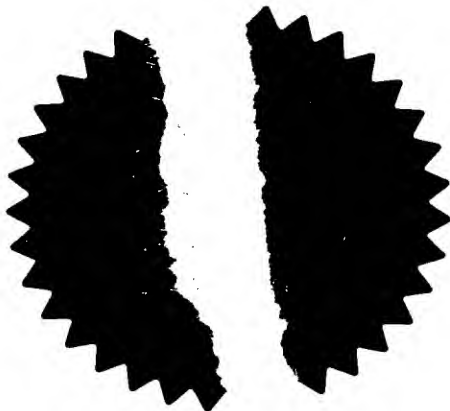


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270CT00 E579078-6 003022

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ENGLAND, UNITED KINGDOM

26 OCT 2000

4141371002

4. Title of the invention

PROCESS

5. Name of your agent (if you have one)

WILSON, Michael John

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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## PROCESS

The present invention relates to a process for the oxidation of a C2 to C4 alkane to produce the corresponding alkene and carboxylic acid and to integrated processes in which the alkene and carboxylic acid are further used as reactants.

5 Carboxylic acids are useful feedstocks for the production of alkenyl carboxylates. Thus, for example, acetic acid is used to manufacture vinyl acetate which is generally prepared commercially by contacting ethylene and acetic acid with molecular oxygen in the presence of a catalyst active for the production of vinyl acetate. Suitably, the catalyst may comprise palladium, an alkali metal acetate promoter and an optional co-promoter  
10 (for example, gold or cadmium) on a catalyst support.

Acetic acid may be produced by the catalytic oxidation of ethylene and/or ethane.

Integrated processes for producing acetic acid and/or vinyl acetate are known in the art. EP-A-0 877 727 discloses an integrated process for the production of acetic acid and/or vinyl acetate in any pre-determined and variable proportions from a gaseous  
15 feedstock comprising ethylene and/or ethane. The integrated process comprises a first step wherein ethylene and/or ethane is catalytically oxidised in a first reaction zone to produce a first product stream comprising acetic acid, water and ethylene and optionally ethane, carbon monoxide, carbon dioxide and/or nitrogen. The acetic acid and ethylene produced in this first reaction zone are then contacted in a second reaction zone with a  
20 molecular oxygen-containing gas in the presence of a catalyst to produce a second product stream comprising vinyl acetate, water, acetic acid and optionally ethylene. No mention is made of any control of the production ratio of ethylene to acetic acid from the catalytic oxidation of ethane and/or ethylene.

Research Disclosure 2244 of 1992(June) No. 338 describes a process for the

oxidation of ethane and/or ethylene to produce acetic acid in which the by-product carbon monoxide is oxidised to carbon dioxide. According to this document, the acetic acid, unreacted ethane (if present) and ethylene is passed with or without carbon dioxide and water removal, to a reactor having a suitable catalyst for the production of ethyl acetate or, with the addition of oxygen, for the production of vinyl acetate. This document is silent on the control of the ratio of ethylene to acetic acid produced in the oxidation step.

In the manufacture of vinyl acetate from ethylene and acetic acid, the molar ratio of the fresh feed ethylene to acetic acid is desirably unity or approximately unity. Thus, in an integrated process in which ethane is oxidised in an oxidation reaction zone to produce ethylene and acetic acid for use in a second reaction zone for the production of vinyl acetate, to maximise overall integrated process efficiency and also vinyl acetate output, the molar ratio of ethylene to acetic acid produced in the oxidation reaction zone, is desirably unity or approximately unity depending upon the selectivity/yield in the second reaction zone.

The effect of water on the formation of acetic acid during the oxidation of ethane to acetic acid is described in US 4250346, but this does not disclose the effect of ethylene on the ratio of products formed.

Thus, there remains a need for a process for the oxidation of a C2 to C4 alkane to produce the corresponding alkene and carboxylic acid in which the molar ratio of alkene to carboxylic acid produced is adjusted or maintained at a pre-determined value.

Accordingly, the present invention provides a process for the oxidation of a C2 to C4 alkane to produce the corresponding alkene and carboxylic acid which process comprises feeding, in one or more feed streams, to an oxidation reaction zone said alkane, an oxygen-containing gas, the corresponding alkene and optionally water and contacting in said oxidation reaction zone, said alkane, oxygen-containing gas, the corresponding alkene and optional water, in the presence of at least one catalyst active for the oxidation of the alkane to the corresponding alkene and carboxylic acid, to produce said alkene and carboxylic acid and water, characterised in that the molar ratio of alkene to carboxylic acid produced in said oxidation reaction zone is adjusted or maintained at a pre-determined value by controlling the amounts of alkene and optional water fed to the oxidation reaction zone.



Each of the alkane, oxygen-containing gas, alkene and water may be introduced into the oxidation reaction zone as fresh feed and/or recycle component

In a further embodiment of the present invention the molar ratio of alkene to carboxylic acid produced in said oxidation reaction zone is adjusted or maintained at a pre-determined value by also controlling one or more of the pressure, temperature and residence time of the oxidation reaction zone.

If the at least one catalyst in the oxidation reaction zone de-activates or otherwise changes its selectivity in use, the molar ratio of alkene to carboxylic acid produced may be maintained at a constant, pre-determined value by controlling the amounts of the alkene and water fed to the oxidation reaction zone and optionally by also controlling one or more of the pressure, temperature and residence time of the oxidation reaction zone.

The present invention also provides a method of adjusting the molar ratio of alkene to carboxylic acid produced, for example in response to changes in demand or requirement in down-stream processes by controlling the amounts of alkene and water fed to the oxidation reaction zone and optionally by also controlling one or more of the pressure, temperature and residence time of the oxidation reaction zone.

The process of the present invention is particularly useful when the alkene and/or carboxylic acid products are used at least in part in integrated downstream processes, for example (a) for the production of ester by reacting the carboxylic acid with the alkene or an alcohol or (b) for the production of alkenyl carboxylate by the reaction of an oxygen-containing gas with the carboxylic acid and alkene. Alkene and/or carboxylic acid may be recovered from the product of the oxidation reaction zone and/or additional alkene and/or carboxylic acid may be used in the down-stream process.

In a further embodiment of the present invention, the alkene and carboxylic acid may be produced in a molar ratio suitable for use in an integrated down-stream process, for example (a) for the production of ester by reacting the carboxylic acid with the alkene or (b) for the production of alkenyl carboxylate by the reaction of an oxygen-containing gas with the carboxylic acid and alkene. If alkene and/or carboxylic acid is neither separately recovered from reaction product nor separately added to the downstream process, the molar ratio of alkene to carboxylic acid produced in the oxidation reaction zone is suitably approximately 1 : 1, for example, 0.8 : 1 to 1.4 : 1. A different ratio may

be produced if alkene and/or carboxylic acid is separately recovered from the oxidation reaction product or separately added to the down-stream process. The molar ratio of alkene to carboxylic acid may then be adjusted by controlling the amounts of the at least one of alkene and water in the total combined feeds to the oxidation reaction zone and optionally by also controlling one or more of the pressure, temperature and residence time of the oxidation reaction zone, for example to meet changes in market demand or feedstock availability. Suitably, the molar ratio of alkene to carboxylic acid produced in the oxidation reaction zone is in the range 1 : 10 to 10 : 1.

Accordingly, the present invention provides an integrated process for the production of an alkyl carboxylate which process comprises the steps :

(a) feeding, in one or more feed streams, to an oxidation reaction zone said alkane, an oxygen-containing gas, the corresponding alkene and optionally water and contacting in said oxidation reaction zone, said alkane, oxygen-containing gas, the corresponding alkene and optional water, in the presence of at least one catalyst active for the oxidation of the alkane to the corresponding alkene and carboxylic acid, to produce said alkene and carboxylic acid and water; and

(b) contacting in a second reaction zone at least a portion of each of said alkene and carboxylic acid produced in the first reaction zone, in the presence of a catalyst active for the production of alkyl carboxylate to produce said alkyl carboxylate,

and in which the molar ratio of alkene to carboxylic acid produced in said oxidation reaction zone is adjusted or maintained at a pre-determined value by controlling the amounts of alkene and water fed to the oxidation reaction zone, and optionally by also controlling one or more of the pressure, temperature and residence time of the oxidation reaction zone.

Also, in another embodiment, the present invention provides an integrated process for the production of an alkenyl carboxylate which process comprises the steps:

(a) feeding, in one or more feed streams, to an oxidation reaction zone said alkane, an oxygen-containing gas, the corresponding alkene and optionally water and contacting in said oxidation reaction zone, said alkane, oxygen-containing gas, the corresponding alkene and optional water, in the presence of at least one catalyst active for the oxidation of the alkane to the corresponding alkene and carboxylic acid, to produce said alkene and carboxylic acid and water; and

(b) contacting in a second reaction zone at least a portion of each of said alkene and carboxylic acid produced in the first reaction zone and a molecular oxygen-containing gas, in the presence of a catalyst active for the production of alkenyl carboxylate to produce said alkenyl carboxylate,

5 and in which the molar ratio of alkene to carboxylic acid produced in said oxidation reaction zone is adjusted or maintained at a pre-determined value by controlling the amounts of alkene and optional water fed to the oxidation reaction zone, and optionally by also controlling one or more of the pressure, temperature and residence time of the oxidation reaction zone.

10 Preferably, the molar ratio of alkene : carboxylic acid produced in the oxidation reaction zone is maintained at approximately 1 : 1, for example, 0.8 : 1 to 1.4 : 1 for subsequent use in a second reaction zone for the production of alkyl carboxylate or alkenyl carboxylate.

15 In the present invention, preferably, the C2 to C4 alkane is ethane, the corresponding alkene being ethylene and the corresponding carboxylic acid being acetic acid. These products may be reacted in down-stream processes to produce ethyl acetate or, with an oxygen-containing gas to produce vinyl acetate.

Typically, the oxidation reaction is performed heterogeneously with solid catalysts and the reactants in the fluid phase. In this case, the amounts of alkene and water may be  
20 controlled as partial pressures in the oxidation reaction zone.

Catalysts active for the oxidation of alkane to alkene and carboxylic acid may comprise any suitable catalysts known in the art, for example, for the oxidation of ethane to ethylene and acetic acid as described in US 4596787, EP-A-0407091, DE 19620542, WO 99/20592, DE 19630832, WO 98/47850, WO 99/51339, EP-A-0 1043064, WO  
25 9913980, US 5300682 and US 5300684, the contents of which are hereby incorporated by reference.

US 4596787 relates to a process for the low temperature oxydehydrogenation of ethane to ethylene using a catalyst having the empirical formula  $\text{Mo}_a\text{V}_b\text{Nb}_c\text{Sb}_d\text{X}_e$  as therein defined, the elements being present in combination with oxygen.

30 EP-A-0407091 relates to process and catalyst for the production of ethylene and/or acetic acid by oxidation of ethane and/or ethylene in the presence of an oxidation catalyst comprising molybdenum, rhenium and tungsten.

DE 19620542 relates to molybdenum, palladium, rhenium based oxidation catalysts for the production of acetic acid from ethane and/or ethylene.

WO 99/20592 relates to a method of selectively producing acetic acid from ethane, ethylene or mixtures thereof and oxygen at high temperature in the presence of a catalyst having the formula  $Mo_aPd_bX_cY_d$  wherein X represents one or several of Cr, Mn, Nb, Ta, Ti, V, Te and W; Y represents one or several of B, Al, Ga, In, Pt, Zn, Cd, Bi, Ce, Co, Rh, Ir, Cu, Ag, Au, Fe, Ru, Os, K, Rb, Cs, Mg, Ca, Sr, Ba, Nb, Zr, Hf, Ni, P, Pb, Sb, Si, Sn, Tl and U and  $a=1$ ,  $b=0.0001$  to  $0.01$ ,  $c = 0.4$  to  $1$  and  $d = 0.005$  to  $1$ .

German patent application DE 196 30 832 A1 relates to a similar catalyst composition in which  $a = 1$ ,  $b > 0$ ,  $c > 0$  and  $d = 0$  to  $2$ . Preferably,  $a = 1$ ,  $b = 0.0001$  to  $0.5$ ,  $c = 0.1$  to  $1.0$  and  $d = 0$  to  $1.0$ .

WO 98/47850 relates to a process for producing acetic acid from ethane, ethylene or mixtures thereof and a catalyst having the formula  $W_aX_bY_cZ_d$  in which X represents one or several of Pd, Pt, Ag and Au, Y represents one or several of V, Nb, Cr, Mn, Fe, Sn, Sb, Cu, Zn, U, Ni, and Bi and Z represents one or several of Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Sc, Y, La, Ti, Zr, Hf, Ru, Os, Co, Rh, Ir, B, Al, Ga, In, Tl, Si, Ge, Pb, P, As and Te,  $a = 1$ ,  $b > 0$ ,  $c > 0$  and  $d$  is  $0$  to  $2$ .

WO 99/51339 relates to a catalyst composition for the selective oxidation of ethane and/or ethylene to acetic acid which composition comprises in combination with oxygen the elements  $Mo_aW_bAg_cIr_dX_eY_f$  wherein X is the elements Nb and V; Y is one or more elements selected from the group consisting of Cr, Mn, Ta, Ti, B, Al, Ga, In, Pt, Zn, Cd, Bi, Ce, Co, Rh, Cu, Au, Fe, Ru, Os, K, Rb, Cs, Mg, Ca, Sr, Ba, Zr, Hf, Ni, P, Pb, Sb, Si, Sn, Tl, U, Re and Pd;  $a, b, c, d, e$  and  $f$  represent the gram atom ratios of the elements such that  $0 < a \leq 1$ ,  $0 \leq b < 1$  and  $a + b = 1$ ;  $0 < (c + d) \leq 0.1$ ;  $0 < e \leq 2$ ; and  $0 \leq f \leq 2$ .

EP-A-1043064 relates to a catalyst composition for the oxidation of ethane to ethylene and/or acetic acid and/or for the oxidation of ethylene to acetic acid which composition comprises in combination with oxygen the elements molybdenum, vanadium, niobium and gold in the absence of palladium according to the empirical formula :  $Mo_aW_bAu_cV_dNb_eY_f$  wherein Y is one or more elements selected from the group consisting of : Cr, Mn, Ta, Ti, B, Al, Ga, In, Pt, Zn, Cd, Bi, Ce, Co, Rh, Ir, Cu, Ag, Fe, Ru, Os, K, Rb, Cs, Mg, Ca, Sr, Ba, Zr, Hf, Ni, P, Pb, Sb, Si, Sn, Tl, U, Re, Te, La and Pd;  $a, b, c, d, e$  and  $f$  represent the gram atom ratios of the elements such that :

0 < a ≤ 1; 0 ≤ b < 1 and a + b = 1; 10<sup>-5</sup> < c ≤ 0.02; 0 < d ≤ 2; 0 < e ≤ 1; and 0 ≤ f ≤ 2.

WO 99/13980 relates to a catalyst for the selective oxidation of ethane to acetic acid of formula: Mo<sub>a</sub>V<sub>b</sub>Nb<sub>c</sub>X<sub>d</sub> wherein X is at least one promoter element selected from the group consisting of P, B, Hf, Te and As; a is a number ranging from about 1 to about 5; b is 1; c is a number ranging from about 0.01 to about 0.5; and d is a number ranging from greater than 0 to about 0.1.

US 5300682 relates to the use of oxidation catalyst with empirical formula of VP<sub>a</sub>M<sub>b</sub>O<sub>x</sub> where M is one or more of Co, Cu, Re, Fe, Ni, Nb, Cr, W, U, Ta, Ti, Zr, Hf, Mn, Pt, Pd, Sn, Sb, Bi, Ce, As, Ag and Au, a is 0.5 to 3, b is 0.1 and x satisfies the valence requirements.

US 5300684 relates to a fluid bed oxidation reaction using for example Mo<sub>0.37</sub>Re<sub>0.25</sub>V<sub>0.26</sub>Nb<sub>0.07</sub>Sb<sub>0.03</sub>Ca<sub>0.02</sub>O<sub>x</sub>.

Other suitable oxidation catalysts for use in the present invention are described in WO 99/13980 which relates to the use of catalysts with elements in combination with oxygen in the relative gram atom ratios of Mo<sub>a</sub>V<sub>b</sub>Nb<sub>c</sub>X<sub>d</sub> where X = P, B, Hf, Te or As; US 6030920 which relates to the use of catalysts with elements in combination with oxygen in the relative gram atom ratios of Mo<sub>a</sub>V<sub>b</sub>Nb<sub>c</sub>Pd<sub>d</sub>; WO 00/00284 which relates to the use of catalysts with elements in combination with oxygen in the relative gram atom ratios of Mo<sub>a</sub>V<sub>b</sub>Nb<sub>c</sub>Pd<sub>d</sub> and/or Mo<sub>a</sub>V<sub>b</sub>La<sub>c</sub>Pd<sub>d</sub>; US 6087297 which relates to the use of catalysts with elements in combination with oxygen in the relative gram atom ratios of Mo<sub>a</sub>V<sub>b</sub>Pd<sub>c</sub>La<sub>d</sub>; WO 00/09260 which relates to the use of catalysts with elements in combination with oxygen in the relative gram atom ratios of Mo<sub>a</sub>V<sub>b</sub>La<sub>c</sub>Pd<sub>d</sub>Nb<sub>e</sub>X<sub>f</sub> where X = Cu or Cr and e and f can be zero; WO 00/29106 and WO 00/29105 which relate to the use of catalysts with elements in combination with oxygen in the relative gram atom ratios of Mo<sub>a</sub>V<sub>b</sub>Ga<sub>c</sub>Pd<sub>d</sub>Nb<sub>e</sub>X<sub>f</sub> wherein X = La, Te, Ge, Zn, Si, In or W and WO 00/38833 which relates to the use of catalysts with elements in combination with oxygen in the relative gram atom ratios of Mo<sub>a</sub>V<sub>b</sub>La<sub>c</sub>Pd<sub>d</sub>Nb<sub>e</sub>X<sub>f</sub> wherein X = Al, Ga, Ge or Si, the contents of which are hereby incorporated by reference.

Solid catalysts active for the oxidation of the C<sub>2</sub> to C<sub>4</sub> alkane may be supported or unsupported. Examples of suitable supports include silica, diatomaceous earth, montmorillonite, alumina, silica alumina, zirconia, titania, silicon carbide, activated carbon and mixtures thereof.

Solid catalysts active for the oxidation of the C2 to C4 alkane may be used in the form of a fixed or fluidised bed.

The oxidation catalyst would be expected to oxidise at least part of any alkene fed to the oxidation reaction zone, for example to the corresponding carboxylic acid.

5       The molecular oxygen-containing gas used in the oxidation reaction zone, may be air or a gas richer or poorer in molecular oxygen than air. A suitable gas may be, for example, oxygen diluted with a suitable diluent, for example nitrogen or carbon dioxide. Preferably, the molecular oxygen-containing gas is oxygen. Preferably, at least some of the molecular oxygen-containing gas is fed to the oxidation reaction zone independently  
10       from the alkane and optional alkene feeds, and any recycle streams.

The alkane and alkene fed into the oxidation reaction zone of the process of the present invention may be substantially pure or may be admixed, for example, with one or more of nitrogen, methane, carbon dioxide, carbon monoxide, hydrogen, and low levels of C3/C4 alkenes/alkanes.

15       Suitably, the amount of alkene (as fresh feed and recycle component) is from greater than 0 and up to and including 50 mol % of the total feed, including recycles, to the oxidation reaction zone, preferably from 1 to 20 mol %, more preferably from 1 to 15 mol %.

20       Suitably, the amount of optional water (as fresh feed and recycle component) is from 0 to 50 mol % inclusive of the total feed, including recycles, to the oxidation reaction zone, preferably from 0 to 25 mol %.

When solid catalysts are used in the oxidation reaction zone alkane, optional alkene, molecular-oxygen containing gas and any recycle gases are preferably passed through the oxidation reaction zone with a residence time corresponding to a combined  
25       gas hourly space velocity (GHSV) of 500-10,000hr<sup>-1</sup>; the GHSV being defined as volume (calculated at STP) of gas passing through the reactor divided by the bulk volume of settled catalyst.

The oxidation reaction of the present invention may suitably be carried out at a temperature in the range from 100 to 400°C, typically in the range 140 to 350°C.

30       The oxidation reaction of the present invention may suitably be carried out at atmospheric or superatmospheric pressure, for example in the range from 80 to 400 psig.

Typically, alkane conversions in the range 1 to 99% may be achieved in oxidation

reaction of the present invention.

Typically, oxygen conversions in the range 30 to 100% may be achieved in the oxidation reaction of the present invention.

In the oxidation reaction of the present invention, the catalyst suitably has a productivity in the range 10 to 10000 grams of carboxylic acid, such as acetic acid, per hour per kilogram of catalyst.

Depending upon the nature of any catalyst used in any downstream process, it is desirable that when used for the production of alkenyl carboxylate, such as vinyl acetate, the first product stream should have a low concentration of carbon monoxide by-product as this may have an adverse effect on some catalysts for the production of alkenyl carboxylates e.g. vinyl acetate. Thus it is preferred to use a catalyst in the oxidation reaction zone that gives negligible carbon monoxide by-product. An additional catalyst component in the oxidation reaction zone may be used to oxidise carbon monoxide to carbon dioxide. This may be present in the oxidation catalyst or catalysts or in a secondary reaction zone.

When ethane is used as reactant for the oxidation process, the product stream comprises acetic acid, ethylene and water, and may contain ethane and oxygen, inert gas components such as argon and nitrogen and the by-products, acetaldehyde, carbon monoxide and carbon dioxide. Acetaldehyde and carbon monoxide may be converted by the molecular oxygen-containing gas to produce acetic acid and carbon dioxide respectively, either in down stream processes or, after recycling, in the oxidation reaction zone. Ethylene is present in the product stream of the oxidation reaction as unconverted reactant ethylene from the feed and/or as oxidation product of the ethane reactant.

The product from the oxidation process may be fed directly or indirectly after one or more separation stages, to a second reaction zone together with optionally additional molecular oxygen-containing gas, optionally additional alkene and optionally additional carboxylic acid to produce alkenyl carboxylate, such as vinyl acetate. Carboxylic acid and/or alkene may be optionally recovered from the product of the oxidation process. Unconverted alkane and/or alkene may be recycled together or after at least partial separation from the downstream process to the oxidation reaction zone directly or indirectly after one or more separation stages.

Catalysts known in the art for the production of alkenyl carboxylates may be used

in the process of the present invention. Thus, catalyst active for the production of vinyl acetate which may be used in a second reaction zone of the present invention may comprise, for example, catalysts as described in GB 1 559 540; US 5,185,308 and EP-A-0672453 the contents of which are hereby incorporated by reference.

5 GB 1 559 540 describes a catalyst active for the preparation of vinyl acetate by the reaction of ethylene, acetic acid and oxygen, the catalyst consisting essentially of:

(1) a catalyst support having a particle diameter of from 3 to 7 mm and a pore volume of from 0.2 to 1.5 ml/g, a 10% by weight water suspension of the catalyst support having a pH from 3.0 to 9.0, (2) a palladium-gold alloy distributed in a surface layer of the  
10 catalyst support, the surface layer extending less than 0.5 mm from the surface of the support, the palladium in the alloy being present in an amount of from 1.5 to 5.0 grams per litre of catalyst, and the gold being present in an amount of from 0.5 to 2.25 grams per litre of catalyst, and (3) from 5 to 60 grams per litre of catalyst of alkali metal acetate.

15 US 5,185,308 describes a shell impregnated catalyst active for the production of vinyl acetate from ethylene, acetic acid and an oxygen containing gas, the catalyst consisting essentially of: (1) a catalyst support having a particle diameter from about 3 to about 7 mm and a pore volume of 0.2 to 1.5 ml per gram, (2) palladium and gold distributed in the outermost 1.0 mm thick layer of the catalyst support particles, and  
20 (3) from about 3.5 to about 9.5% by weight of potassium acetate wherein the gold to palladium weight ratio in said catalyst is in the range 0.6 to 1.25.

EP-A-0672453 describes palladium containing catalysts and their preparation for fluid bed vinyl acetate processes.

An advantage of using a palladium-containing catalyst is that any carbon monoxide  
25 produced in the first reaction zone will be consumed in the presence of oxygen and the palladium-containing catalyst in the second reaction zone, thereby eliminating the need for a separate carbon monoxide removal reactor.

Typically, the production of alkenyl carboxylate such as vinyl acetate in the second reaction zone is carried out heterogeneously with the reactants being present in the gas  
30 phase.

Additional alkene reactant may be fed to the second reaction zone for the production of alkenyl carboxylate as well as the alkene from the oxidation reaction zone



as oxidation product and/or unconsumed alkene reactant.

Additional alkene introduced into the second reaction zone for the production of alkenyl carboxylate may be substantially pure or may be admixed, for example, with one or more of nitrogen, methane, carbon dioxide, carbon monoxide, hydrogen, and low levels of C3/C4 alkenes/alkanes.

The molecular oxygen-containing gas used in the second reaction zone for the production of alkenyl carboxylate may comprise unreacted molecular oxygen-containing gas from step (a) and/or additional molecular oxygen-containing gas.

The additional molecular oxygen-containing gas, if used, may be air or a gas richer or poorer in molecular oxygen than air. A suitable additional molecular oxygen-containing gas may be, for example, oxygen diluted with a suitable diluent, for example nitrogen or carbon dioxide. Preferably, the additional molecular oxygen-containing gas is oxygen. Preferably, at least some of the molecular oxygen-containing gas is fed independently to the second reaction zone from the alkene and carboxylic acid reactants.

At least part of the carboxylic acid fed to the second reaction zone may be liquid.

When solid catalysts are used in the second reaction zone for the production of alkenyl carboxylate, the product from the oxidation reaction zone, any additional alkene or carboxylic acid reactants, any recycle streams and molecular oxygen-containing gas are preferably passed through the second reaction zone at a combined gas hourly space velocity (GHSV) of 1000-10,000hr<sup>-1</sup>.

The second reaction zone for the production of alkenyl carboxylate may suitably be operated at a temperature in the range from 140 to 200°C.

The second reaction zone for the production of alkenyl carboxylate may suitably be operated at a pressure in the range 50 to 300 psig.

The second reaction zone for the production of alkenyl carboxylate may suitably be operated as either a fixed or a fluidised bed process.

Carboxylic acid conversions in the range 5 to 80% may be achieved in the second reaction zone for the production of alkenyl carboxylate.

Oxygen conversions in the range 20 to 100% may be achieved in the second reaction zone for the production of alkenyl carboxylate.

Alkene conversions in the range 5 to 100% may be achieved in the second reaction zone for the production of alkenyl carboxylate.

In the second reaction zone for the production of alkenyl carboxylate, the catalyst suitably has a productivity in the range 10 to 10000 grams of alkenyl carboxylate per hour per kg of catalyst.

When the alkane used in the process of the present invention is ethane, the product stream from the second reaction zone for the production of alkenyl carboxylate may comprise vinyl acetate, water and acetic acid and optionally also unreacted ethylene, ethane, acetaldehyde, nitrogen, argon, carbon monoxide and carbon dioxide. Such a product stream may be separated by azeotropic distillation into an overhead fraction comprising vinyl acetate and water and a base fraction comprising acetic acid and water. The base fraction may be removed from the distillation column as liquid from the bottom of the column, or as a vapour one or more stages above the bottom of the column. Prior to such a distillation step, ethylene, ethane, acetaldehyde, carbon monoxide and carbon dioxide, if any, may be removed from the second product stream, suitably as an overhead gaseous fraction from a scrubbing column, in which a liquid fraction comprising vinyl acetate, water and acetic acid is removed from the base. The ethylene and/or ethane may be recycled to step (a) and/or step (b).

Vinyl acetate is recovered from the overhead fraction, suitably for example by decantation. The recovered vinyl acetate may, if desired, be further purified in known manner.

The base fraction comprising acetic acid and water may be recycled, with or preferably without further purification, to step (b) of the process. Alternatively, acetic acid is recovered from the base fraction and may be further purified if desired, in known manner, for example by distillation.

A suitable process for the production of esters by reaction of the carboxylic acid with the alkene is described in EP-A-0926126, the contents of which are hereby incorporated by reference and which relates to an esterification process comprising reacting in an addition reaction a lower olefin with a saturated lower aliphatic monocarboxylic acid in the vapour phase in the presence of a heteropolyacid catalyst characterised in that the reaction is carried out in a plurality of reactors set up in series such that the gases comprising the unreacted gases and products exiting from a first reactor are fed as the feed gas to a second reactor and those exiting from the second reactor are fed as feed gas to the third reactor and so on for the subsequent reactors, and

an aliquot of the reactant monocarboxylic acid is introduced into the feed gas to each of the second and subsequent reactors so as to maintain the olefin to monocarboxylic acid ratio in the feed gas to each of the second and subsequent reactors within a pre-determined range.

5 The invention will now be illustrated by way of example only and with reference to the Figure and to the following examples.

The Figure represents in schematic block-diagram, apparatus suitable for use in the process of the present invention.

10 The apparatus comprises an oxidation reaction zone (1) provided with a supply of ethane and optionally ethylene (3), a supply of a molecular oxygen-containing gas (4), a supply of recycle gas comprising ethane and ethylene (5) and an outlet (18) for a first product stream. Depending on the scale of the process, the oxidation reaction zone (1) may comprise either a single reactor or several reactors in parallel or series.

15 The apparatus also comprises a second reaction zone (2) for acetoxylation of ethylene to vinyl acetate which is provided with means (17) for conveying at least a portion of the product from the first reaction zone into the second reaction zone, a supply of molecular oxygen-containing gas (9), a supply of recycle acetic acid (10) and an optional supply or supplies of ethylene and/or acetic acid (8). Depending on the scale of the process, the second reaction zone (3) may comprise either a single reactor or  
20 several reactors in parallel or in series.

The apparatus further comprises an optional scrubber (6) for the first reaction product; a scrubber (12) for the product from the second reaction zone; means (13) for separating acetic acid from the product of the second reaction zone; vinyl acetate purification means (14); optional acetic acid purification means (15) and one or more  
25 separation means (16) for separating carbon dioxide from recycle gases from the second reaction zone and optionally for recovery of ethylene product.

30 In use, the oxidation reaction zone (1) is provided with at least one catalyst each active for the oxidation of the ethane to form acetic acid and ethylene. Suitably the oxidation catalysts are solid catalysts. Molecular oxygen-containing gas is fed to the oxidation reaction zone (1) from supply (4) through one or more inlets. A gaseous feedstock comprising ethane, and optionally ethylene is fed to the oxidation reaction zone (1) from supply (3). Recycle gas comprising ethane and ethylene is also fed to the

oxidation reactor from supply (5). The molecular oxygen-containing gas, ethane and recycle gas are introduced into the oxidation reaction zone through one or more inlets separately or in partial or complete combination. Optionally at least one of the streams fed to the oxidation reactor also comprises water.

5 In the oxidation reactor a first product stream is produced which comprises ethylene (as product and/or unreacted feed), acetic acid, water, optionally unconsumed molecular oxygen-containing gas and by-products such as carbon monoxide, carbon dioxide, inerts and acetaldehyde. This may optionally be passed to a scrubber (16) from which gas and liquid are removed. The gas may be recycled after separating by-products  
10 such as carbon dioxide and optionally recovering ethylene product by methods known in the art. Acetic acid may be recovered from the liquid, for example by distillation.

At least a portion of the first product stream is fed by means (17) into the second reaction zone which is provide with an acetoxylation catalyst, suitably a solid catalyst.

A molecular oxygen-containing gas is fed to the second reaction zone from supply  
15 (9). Acetic acid is fed to the second reaction zone from recycle supply (10). Optionally, additonal ethylene and/or acetic acid may be fed to the second reaction zone from supply or supplies (8). The first product stream, molecular oxygen-containing gas, recycle acetic acid and optional additional supplies of ethylene and/or acetic acid are fed into the second reaction zone through one or more inlets separately or in partial or complete  
20 combination.

In the second reaction zone the ethylene, acetic acid and molecular oxygen react to produce a second product stream comprising vinyl acetate.

The second reaction product is passed to scrubber (12) from which gas and liquid are separated. Carbon dioxide is separated from the gas and optionally ethylene product  
25 recovered, in one or more separation stages (16) by methods known in the art. The remaining ethylene and ethane may be recycled to the first and/or second reactors. Acetic acid is separated from the scrubber liquid and is recycled to the second reaction zone. Optionally, acetic acid product may be recovered from the recycle stream by means (15), for example by distillation. Vinyl acetate product is recovered from the  
30 scrubber liquid by means (14), for example by distillation.

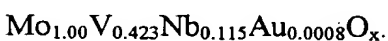
In use, if selectivity of the at least one catalyst in the oxidation reaction zone changes, for example by deactivation, the molar ratio of alkene to carboxylic acid

produced in the oxidation reaction zone is adjusted or maintained at a pre-determined value by controlling the amounts of alkene and water fed to the oxidation reaction zone and optionally by also controlling one or more of the pressure, temperature and residence time of the oxidation reaction zone.

Preferably, the molar ratio of ethylene: acetic acid produced in the oxidation reaction zone is maintained at approximately 1 : 1, for example, 0.8 : 1 to 1.4 : 1 for subsequent use in the second reaction zone for the production of vinyl acetate. A different ratio may be maintained if ethylene and/or acetic acid is separately recovered from the oxidation reaction product or separately added to the second reaction zone for the production of vinyl acetate. The molar ratio of ethylene to acetic acid may then be adjusted by controlling the amounts of the alkene and water fed to the oxidation reaction zone and optionally by also controlling one or more of the pressure, temperature and residence time of the oxidation reaction zone, for example to meet changes in market demand or feedstock availability.

#### **Preparation of catalyst active for ethane oxidation (Catalyst A)**

A solution was prepared by dissolving 45.88 g ammonium molybdate, 12.86 g ammonium vanadate, 8.10 g niobium chloride, 0.0713 g ammonium gold tetrachloride and 6.75 g oxalic acid in 400 ml water heated to 70°C with stirring. After 15 minutes, the solution water was heated to boiling point followed by evaporation to dryness over 2 hours. The resulting catalyst cake was ground and then calcined in static air in an oven at 400°C for 5 hours. The nominal empirical formula of the catalyst was :



#### **General Ethane Oxidation Reaction Method.**

Typically 5 ml of powdered catalyst A was mixed with 15 ml of glass beads of diameter 0.4 mm to form a diluted catalyst bed of 20 ml in volume. The diluted catalyst was then loaded into a fixed bed reactor made of Hastelloy of dimensions 12 mm internal diameter and length 40 cm. The catalyst was maintained in position in the centre of the reactor using quartz wall plugs together with inert packing material above and below the catalyst bed. The apparatus was then pressure-tested at 20 bar with helium to check for leaks. Catalyst A was then activated by heating to 220°C at 5°C/min in helium at 21 bar for 4 hours, to ensure full decomposition of catalyst precursors.

The required flows of ethane, ethylene, 20 % oxygen in helium and water were then introduced to the reactor, to ensure the required inlet composition. This composition was typically in the range 42-57 % v/v ethane, 6.6 % oxygen, 0-20 % v/v ethylene, 0-25 % v/v water and balance helium. The total feed flow rate was maintained at a level to ensure a feed GHSV of 2000-9000/h. After equilibrating for 60 minutes, gas samples were taken from the outlet stream to a GC system (model Unicam 4400) to quantify ethane, ethylene, oxygen and helium.

The setpoint temperature of the reactor was increased until 50-75 % oxygen conversion was achieved, as indicated by the calculated level of oxygen in the outlet stream. Following an further equilibration period of 60 minutes, catalyst A was then evaluated under steady state conditions for a period of typically 4-5 hours. Exit gas volume was measured over the run period by a water-gas meter. Liquid products were collected and weighed after the run period. Composition of gas and liquid products was measured using GC analysis (Unicam 4400 and 4200 fitted with TCD and FID detectors respectively).

From analysis of the feed and product flow rates and compositions the following parameters were calculated :

$$\text{ethane conversion} = (\text{inlet mol ethane} - \text{outlet mol ethane}) / \text{inlet mol ethane} * 100$$

$$\text{oxygen conversion} = (\text{inlet mol oxygen} - \text{outlet mol oxygen}) / \text{inlet mol oxygen} * 100$$

$$\text{selectivity to acetic acid (C-mol \%)} = \frac{(\text{outlet mol acetic acid} * 2)}{(\text{mol ethane converted} * 2)} * 100$$

$$\text{selectivity to ethylene (C-mol \%)} = \frac{(\text{outlet mol ethylene} - \text{inlet mol ethylene}) * 2}{(\text{mol ethane converted} * 2)} * 100$$

$$\text{selectivity to CO (C-mol \%)} = (\text{outlet mol CO}) / (\text{mol ethane converted} * 2) * 100$$

$$\text{selectivity to CO}_2 \text{ (C-mol \%)} = (\text{outlet mol CO}_2) / (\text{mol ethane converted} * 2) * 100$$

STY (space time yield) % = (g acetic acid) / kg catalyst bed / hour

Typically, mass balance and carbon balance for a reaction was found to be 100 +/- 5 %.

In the following experiments the catalyst used was prepared according to the procedure described above, but the catalysts were not necessarily all from the same batch.

#### Example 1.

- 10 In this example varying amounts of ethylene were utilised as feedstock in the general reaction method above. No water was used. The results are shown in Table I below.

Table I

Ethylene (mol %)	Ethane Conversion %	Oxygen Conversion %	Ethylene Sel. %	COx Sel. %	Acetic acid Sel. %	STY Acetic acid G/kg-cat/h
0	11.4	76.8	76.6	10.8	12.6	60.2
5	8.6	57.2	75.9	5.8	18.3	60.5
10	7.5	56.7	64.6	12.3	23.1	58.0
15	5.9	38.7	29.3	57.7	28.4	47.2

- 15 Process conditions : 300°C, 16 bar, 3200/h, 42-57 % ethane, 6.6 % oxygen, 0-15 % ethylene, balance helium.

From the above Table I it can be seen that at a level of 15 mol% ethylene in the reaction mixture, the molar ratio of ethylene to acetic acid reaches approximately unity.

#### 20 Example 2 (comparison).

In this experiment, water in varying amounts was utilised in the above general reaction method. This is not an example according to the present invention because no ethylene was used in the feed. The results are given in Table 2 below.

25

Table 2

Water	Ethane	Oxygen	Ethylene	COx	Acetic	STY Acetic
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(mol %)	Conversion %	Conversion %	Sel. %	Sel. %	acid Sel. %	acid g/kg-cat/h
0	11.4	76.8	76.6	10.8	12.6	60.2
5	9.9	64.5	70.6	5.9	23.5	86.6
15	14.4	97.3	65.7	7.4	27.0	131.7
25	10.5	66.8	50.1	5.6	44.3	145.7

Process conditions : 300°C, 16 bar, 3200/h, 42-57 % ethane, 6.6 % oxygen, 0-25 % water, balance helium.

From Table 2 it can be seen that 25 mol % water has to be used in the feed stream, to achieve a molar ratio of ethylene to acetic acid of approximately unity.

### Examples 3-5.

In these examples ethylene and water were co-fed in the general reaction method. The process conditions employed are shown in Table 3. The results are given in Table 4.

Table 3

Example	Temp (deg.C)	Pressure (barg)	GHSV (1/h)	Contact time (secs)	Ethane (mol %)	Oxygen (mol %)	Ethylene (mol %)	Water (mol %)
3	281	16	3200	8.9	52	6.6	5	10
4	299	22	3200	11.8	52	6.6	10	5
5	300	16	3200	8.6	52	6.6	10	5

Table 4

Example.	Ethane Conversion %	Oxygen Conversion %	Ethylene Sel. %	COx Sel. %	Acetic acid Sel. %	Ethylene/ Acetic acid Ratio	STY Acetic acid g/kg-cat/h
3	8.9	54.4	45.1	6.0	48.8	0.92	162.9
4	11.3	99.6	42.4	12.8	44.8	0.95	197.3
5	12.2	99.6	44.9	14.3	40.8	1.10	175.1

Table 4 shows that the molar ratio of ethylene to acetic acid is approximately 1 to 1 in each of Examples 3-5.



The results of the above Examples 1-5 show that the molar ratio of ethylene to acetic acid produced in the first reaction zone can be adjusted or maintained at a pre-determined value by controlling the amounts of ethylene and water fed to the oxidation reaction zone under different reaction conditions, and in particular a ratio of about unity may be achieved.

#### Examples 6 – 14

Further reactions were performed at different temperatures and pressures to show the effect of these parameters on the ratio of ethylene : acetic acid. The results are shown in Table 5 below. The results below shows the effect of varying pressure and temperature on the performance of catalyst A. Thus, a comparison for the ethylene : acetic acid ratio for Examples 6, 9 and 12 shows that reducing pressure increases the ratio of ethylene : acetic acid. A similar trend is seen in general at different temperatures for Examples 7, 10 and 13 and for Examples 8, 11 and 14.. A comparison of examples 6, 7 and 8 shows that at 22 bar reducing temperature increases the ratio ethylene : acetic acid but decreases it at 9 bar. The results show that the selectivity ratio of ethylene to acetic acid can be adjusted by controlling temperature and/or pressure.

Table 5

Conditions : 3200/h Total feed : 52 mol. % ethane, 6.6 mol. % oxygen, 10 % mol. ethylene, 5 mol. % water, balance helium.

Example No.	Temperature Deg. C	Pressure bara	Ethane Conversion %	Oxygen Conversion %	Ethylene Selectivity C-mol %	COx Selectivity C-mol %	Acetic acid Selectivity C-mol %	Ethylene : acetic acid Selectivity ratio	STY Acetic acid g/kg-cat/h
6	299	22	11.3	99.6	42.4	12.8	44.8	0.95 : 1	197.3
7	291	22	7.4	86.8	44.3	18.1	37.6	1.18 : 1	103.1
8	281	22	6.6	71.3	47.4	13.7	38.9	1.22 : 1	92.4
9	300	16	12.2	99.6	44.9	14.3	40.8	1.10 : 1	175.1
10	291	16	9.3	87.8	44.2	13.5	42.3	1.04 : 1	148.9
11	281	16	6.9	61	48.0	11.1	40.9	1.17 : 1	104.6
12	299	9	6.6	64.2	63.3	9.7	27.0	2.35 : 1	66.7
13	290	9	5.3	46.4	60.6	9.4	30.0	2.02 : 1	61.3
14	280	9	4.6	34.6	58.5	4.8	36.7	1.59 : 1	62.0

FIG.

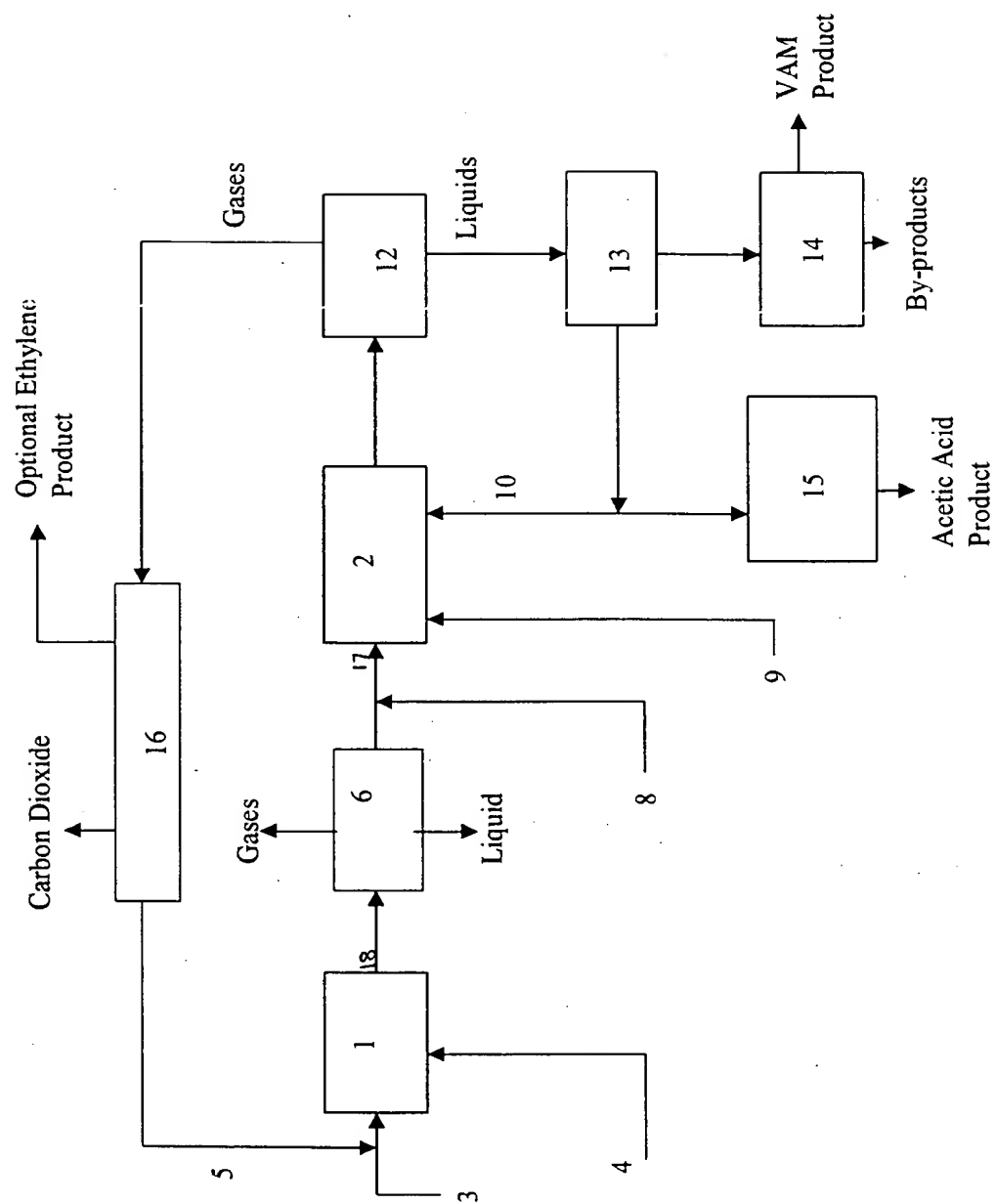




Figure 1. The effect of the concentration of the *Agrobacterium* suspension on the transformation efficiency of *Agrobacterium* strains. The *Agrobacterium* strains were cultured in the YEA medium for 24 h and then adjusted to the concentration of  $1 \times 10^8$  cells/ml. The *Agrobacterium* strains were then cultured in the YEA medium with the concentration of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 cells/ml. The transformation efficiency was determined by the number of transformants per cell. The results are shown in Table 1.